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Teck Cominco Alaska Incorporated

IN THE UNITED STATES DISTRICT COURT  
FOR THE DISTRICT OF ALASKA

KIVALINA RELOCATION PLANNING	)	
COMMITTEE,	)	
	)	
Plaintiff,	)	
	)	
v.	)	Case No. A02-231 CV (JWS)
	)	
TECK COMINCO ALASKA	)	
INCORPORATED and NANA	)	
REGIONAL CORPORATION, INC.,	)	
	)	
Defendants.	)	DECLARATION OF MICHAEL M. BOTZ
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I, MICHAEL M. BOTZ, under penalty of perjury under the laws of the State of Alaska, hereby declare that the following is true and correct:

**Qualifications**

1. I am a registered professional chemical engineer currently employed by Elbow Creek Engineering, Inc., an engineering consulting firm. I hold a Bachelor of Science degree in Chemical Engineering from Montana State University and a Master of Science degree in Chemical Engineering from Purdue University.

2. I have over the last decade worked on projects for over 40 mining and mineral processing sites in North America, Latin America, Europe, Australia, Africa and Asia relating to cyanide chemistry and treatment. In addition to industrial project work, I have provided course instruction to academic, government and industry persons, and have presented research findings at mining industry professional societies. I am a member of the American Institute of Chemical Engineers (AIChE), the Society for Mining, Metallurgy and Exploration (SME) and the American Water Works Association (AWWA), and have presented papers and chaired sessions specifically dealing with the environmental management of water and cyanide.
  
3. I have authored and co-authored over 20 technical papers in regard to the management and treatment of cyanide and its associated compounds. I was the co-editor and authored technical papers in the text *The Cyanide Monograph* and was co-author of the book *Chemistry and Treatment of Cyanidation Wastes (2<sup>nd</sup> Edition)*, both published through Mining Journal Books Ltd. in London, England, and co-edited the recently released compact disc titled *The Cyanide Compendium*, containing over 1,000 pages of information regarding cyanide and its chemistry, analysis, environmental fate, toxicity, management, recovery and treatment.

## **Cyanide and Analytical Methods to Measure its Concentration in Solutions**

4. The term “cyanide” refers to a molecule containing one atom of carbon and one atom of nitrogen connected by a triple bond ( $\text{--C}\equiv\text{N}$ ). In solution, cyanide may be present as “free cyanide” or in complexed form with metals such as copper, iron or zinc. The free forms of cyanide, which include molecular hydrogen cyanide ( $\text{HCN}$ ) and its anion ( $\text{CN}^-$ ), have been traditionally considered as the most important from a toxicological and regulatory standpoint. The United States Environmental Protection Agency (EPA) Ambient Water Quality Criteria document for cyanide notes that the toxicity of cyanide is due to the presence of free cyanide and that the metal cyanide complexes, particularly those of iron, are much less toxic. It was further noted by EPA in this document that measurement of free cyanide would provide a scientifically correct basis for monitoring compliance with aquatic life criteria. Currently, USEPA national water quality guidelines (“National Recommended Water Quality Criteria, Federal Register, Vol. 63, No. 237, pp. 68354-68364, December 10, 1998) provide recommended levels of free cyanide in regard to protecting aquatic life and these levels have been adopted by many regional and state permitting agencies as numerical standards.
5. The measurements of cyanide most often discussed from a monitoring and compliance standpoint include free cyanide, weak acid dissociable (WAD) cyanide and total cyanide. The general relationship between these measurements of cyanide is illustrated in Figure 1 below.

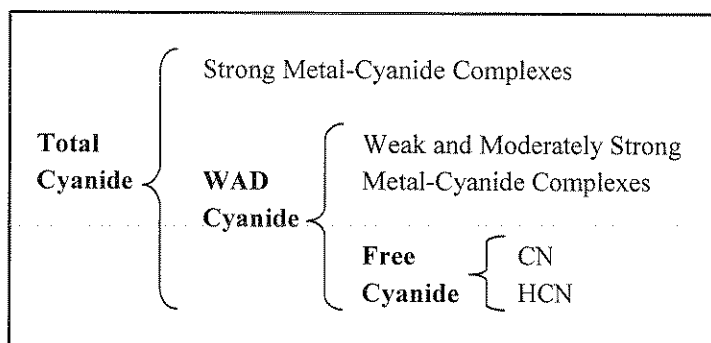


Figure 1  
Relationship Between Free, WAD and Total Cyanide Measurements

### Free Cyanide

6. Of the various measurements of cyanide, “free cyanide” is the primary concern in regard to aquatic toxicity and the USEPA has written its national surface and potable water quality standards in terms of free cyanide (“National Primary Drinking Water Standards, EPA 816-F-02-013, July 2002, and USEPA 1998, referred to in para. 4 above). Free cyanide consists of the uncomplexed forms of cyanide, which are molecular hydrogen cyanide (HCN) and its anion (CN). The difficulty in measuring free cyanide at low levels has long been recognized by the EPA. Standards for environmental protection are below levels at which free cyanide can be reliably quantified and therefore other analytical methods are required to measure cyanide in effluent samples, such as the total cyanide and WAD cyanide analytical methods.

## **Total Cyanide**

7. The most common “total cyanide” analytical methods employed for compliance and general monitoring purposes involve distillation under boiling and strongly acidic conditions. During the distillation, free and metal complexed forms of cyanide are converted to the volatile hydrogen cyanide (HCN) form, which is volatilized from solution and recaptured in a separate caustic absorber. The caustic solution in the absorber is then subjected to a colorimetric analysis to indirectly measure the cyanide concentration in the original sample. Total cyanide analytical procedures provide an indirect measurement of cyanide, unlike direct measurements such as atomic absorption spectrophotometry that may be employed to analyze for metals.

In addition to free cyanide, total cyanide analytical methods in part or entirely quantify cyanide bound to several metals including iron, copper, mercury, nickel and zinc. Some of the metal cyanide complexes, such as those of iron, are very stable chemically. As a result, use of this method for compliance and monitoring purposes may result in an overestimation of the concentration of free cyanide, a problem recognized by the EPA for many years.

## **Weak Acid Dissociable (WAD) Cyanide**

8. Analytically, the “toxicologically significant” or “ecologically important” forms of cyanide are differentiated most accurately from all others by the weak acid dissociable (WAD) cyanide methods. The WAD cyanide procedures measure

free and metal-complexed cyanides, excluding only very stable complexes, such as the iron-cyanides. In the WAD cyanide procedures, a high temperature distillation similar to that described for total cyanide is conducted, however the procedures involve a more moderate pH of about 4.5. The EPA does not have its own analytical procedure for analyzing WAD cyanide by distillation but utilizes those published by *Standard Methods* or the American Society for Testing and Materials.

### **Analytical Variability**

9. There is inherent error associated with every analytical measurement, with errors particularly pronounced at levels near the detection limit. Such error may arise from several random and systematic sources including sampling, preservation, chemical interferences, instruments, sample storage, analytical reagents, equipment cleanliness and analyst proficiency. In addition, there are several natural and manmade compounds that may be present in samples that can interfere with an analysis, producing both positive and negative errors that could possibly lead to measured cyanide levels either higher or lower than the actual concentration.
10. Analytical interference occurs when compounds in a sample other than those being measured influence the results. Known chemical interferences with cyanide analytical methods include the following:

- Thiocyanate

- Sulfide
- Oxidizing agents
- Nitrate and nitrite
- Aldehydes
- Glucose and other sugars
- Carbonate
- Fatty acids

EPA studied the effects of interfering agents on the analysis of total cyanide and found that when multiple interfering agents are present, total cyanide analytical methods produced questionable results and that the effect of interferences was complex.

11. In 1997, EPA completed a comprehensive analytical study that included an approved EPA total cyanide distillation method. The research evaluated the accuracy and precision of the method under varying conditions and included the measurement of both individual metal-cyanide compounds and synthetically prepared wastewater samples. A primary goal of the research was to examine the effects of various interfering agents, such as sulfide and thiocyanate, on the reliability of analytical results. An overall conclusion of the study was that analytical methods used to measure total cyanide in complex chemical matrices “are not only not well validated, in many cases they are highly inaccurate” and that the methods exhibited “severe inaccuracy under a variety of conditions”.

The problems noted were fundamentally related to the presence of one or more potentially interfering substances and the manner in which they can react with various cyanide compounds. The 1997 EPA study also found that methods used to remove the interferences did not work particularly well in improving the analytical results. The recovery of cyanide from its metal complexes was not quantitative and the study concluded that the total cyanide method was "plagued by many problems that led to poor overall performance" and that "in some cases, the actual concentration of cyanide was an insignificant factor to the concentration determined by the method." The problems included the failure to correctly identify the presence of interferences, the inability to remove interferences once identified, and the possibility of interactions between interferences masking one other that proceed at varying rates leading to both positive and negative impacts on reported cyanide values. A suggestion was made that alternative analytical methods should be used to quantify total cyanide in industrial effluents since the approved method was found to be "dysfunctionate as written."

12. Many mining effluents contain thiocyanate, which can break down during distillation and yield a false positive or a higher than expected level of cyanide. There is no approved methodology to remove thiocyanate from samples prior to analysis to preclude its potential effect as an interfering agent. The Red Dog effluent contains approximately 5 to 10 mg/L of thiocyanate, and at this level, thiocyanate could interfere with cyanide analytical methods.



13. Nitrate and nitrite can also affect cyanide analyses, since nitrite can form hydrogen cyanide by reacting with both man-made and natural organic compounds during distillation, and nitrate can be reduced to nitrite under anaerobic conditions thereby indirectly leading to hydrogen cyanide formation. There is no approved methodology to remove nitrate/nitrite from samples prior to analysis, instead analytical reagents are used in an attempt to minimize the potential for nitrate/nitrite interferences. The Red Dog effluent contains approximately 0.5 to 2 mg/L N nitrate plus nitrite, and at this level, nitrate/nitrite could interfere with cyanide analytical methods.
14. When developing aquatic life criteria for cyanide, the EPA recognized that commercial analytical methods were not available to accurately measure free cyanide at low levels. As a result, the EPA initially recommended use of the approved total cyanide analytical procedures when monitoring effluents for compliance purposes. The total cyanide analytical procedures measure free cyanide, but also include several metal-cyanide complexes, including the relatively non-toxic iron cyanides. Recognizing that this approach was overly conservative, the EPA began utilizing the cyanide amenable to chlorination (CATC) method, which does not measure cyanide bound to iron but is limited in its ability to quantify cyanide at the EPA levels for environmental protection.
15. Recently, regulatory agencies in the United States and abroad have adopted weak acid dissociable (WAD) cyanide as the preferred measure of cyanide in effluents, replacing other analytical methods for compliance and general

monitoring. Use of WAD cyanide for these purposes is suitable for measuring the "toxicologically significant" or "environmentally important" forms of cyanide.

16. Presently, NPDES effluents nationwide are regulated using either the total, CATC or WAD cyanide analytical methods. EPA has recommended that certain sites substitute WAD cyanide for total cyanide for monitoring and reporting purposes due to its reliability and the well known variability associated with low-level total cyanide analyses. As of 2002, WAD cyanide analytical methods had been incorporated into 345 NPDES permits nationwide, and the State of Alaska recently modified its water quality regulations to utilize WAD cyanide rather than total cyanide as the means of monitoring compliance with water quality criteria (ADEC "Alaska Water Quality Criteria Manual for Toxic and Other Deleterious Organic and Inorganic Substances," Amended August 2002, Adopted March 2003).
17. The WAD cyanide analytical procedures measure free and metal-complexed cyanides, excluding only the very stable complexes, such as the iron-cyanides. For the Red Dog effluent, WAD cyanide analyses provide a suitable measurement of the cyanide compounds that could potentially exhibit toxicity to aquatic life. Due to the milder reaction conditions in the WAD cyanide analytical procedures in comparison to the total cyanide analytical procedures, WAD cyanide analyses are generally less affected by interferences and generally yield more stable and reproducible results.

18. Teck Cominco provided me with results of WAD cyanide analyses of split samples collected between 1998 and 2002 for NPDES Outfall 001. These were identified to me as splits of the same samples collected and analyzed under the NPDES permit for total cyanide. The WAD cyanide analyses of Outfall 001 were all less than 9 µg/L during this period, except for one sample analyzed from June 2000 with a reported WAD cyanide level of 10 µg/L. Analysis of a split of this same June 2000 effluent sample by another laboratory yielded an analytical result of <2.4 µg/L for WAD cyanide.

#### **Use and Need for MDLs, MLs and IMLs**

19. The EPA stated in Section I.A.5. of the Red Dog NPDES permit that the monthly average total cyanide effluent limitation is not quantifiable using approved analytical methods, and therefore an Interim Minimum Level (IML) of 9 µg/L was selected for total cyanide. According to EPA, the Interim Minimum Level is the lowest concentration at which a particular constituent can be reliably quantified. The Interim Minimum Level should be derived using established EPA calculation procedures, however the basis or justification for selection of the Red Dog Interim Minimum Level for total cyanide was not given in the NPDES permit or corresponding Fact Sheet and it does not appear that established EPA procedures were used in its derivation.
20. The Method Detection Limit (MDL) is used by EPA to indicate the lowest level at which a constituent can be reliably detected in a sample. However, the error of analytical measurements made near the Method Detection Limit is too high to

allow assignment of an accurate numerical value to the measured concentration. Therefore, analytical measurements made near the Method Detection Limit are often designated as “detected but not quantifiable”. At a concentration above the Method Detection Limit, the Minimum Level (or Interim Minimum Level) is used to indicate the lowest concentration at which a constituent can be quantified in a sample such that a reliable numerical value can be assigned to the analytical measurement. The relationship between the Method Detection Limit and Minimum Level is illustrated in Figure 2.

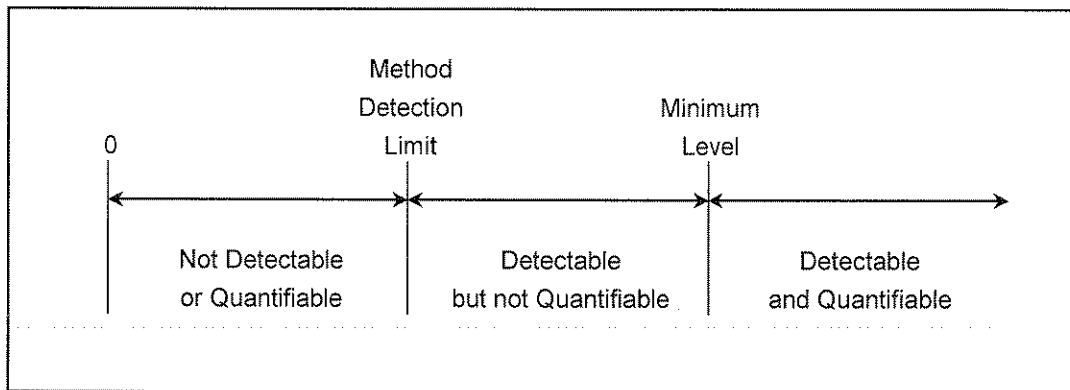


Figure 2  
Relationship Between the Method Detection Limit and Minimum Level

21. In June 2003, Teck Cominco collected several water samples from streams near the Red Dog site that are not influenced by mine discharges and are representative of background conditions near the site. These samples were analyzed for total and WAD cyanide by three commercial laboratories and a summary of the analytical results is presented in Table 1. At these background locations, total cyanide was measured at levels of up to 8 µg/L and WAD cyanide

was measured at levels of up to 4 µg/L. These data illustrate that cyanide analytical data generated from samples collected at the Red Dog site must be viewed in terms of appropriate detection and quantitation limits.

Table 1  
Results of Background Cyanide Analyses at the Red Dog Mine

Sampling Date		Background Location					
		Station 3		Station 9		Station 12	
		Total Cyanide (µg/L)	WAD Cyanide (µg/L)	Total Cyanide (µg/L)	WAD Cyanide (µg/L)	Total Cyanide (µg/L)	WAD Cyanide (µg/L)
June 5, 2003	Lab 1					<3	<3
	Lab 3					<0.6	3
June 7, 2003	Lab 1			<3	<3		
	Lab 3	6	<3	8	2		
June 10, 2003	Lab 3			2	4	5	3
June 15, 2003	Lab 2			<5	<5	<5	<5
June 16, 2003	Lab 3	2	3				

22. Teck Cominco provided me with preliminary analytical data obtained in 2003 from a study conducted in regard to the variability of total cyanide analyses with Outfall 001 samples. Among the laboratories that participated in this study were Columbia Analytical Services and CT&E, the two that had provided Teck Cominco with NPDES related total cyanide analytical data from 1998 through 2002. While many different analyses and studies of interferences were completed by these two laboratories, one part of the study involved multiple analyses of splits from the same Outfall 001 sample for total cyanide using approved analytical methods. Results from analysis of these split samples provide valuable insight into the variation in Outfall 001 total cyanide measurements. Total cyanide measurements reported by one laboratory ranged from 1.5 µg/L to 53 µg/L, while total cyanide measurements reported by the other

laboratory ranged from 5 µg/L to 57 µg/L, all analysis being done using splits of the same Outfall 001 sample. These ranges are illustrated on Figure 3 relative to the 1998-2002 Outfall 001 Red Dog NPDES monitoring data and the 9 µg/L Compliance Evaluation Level for total cyanide.

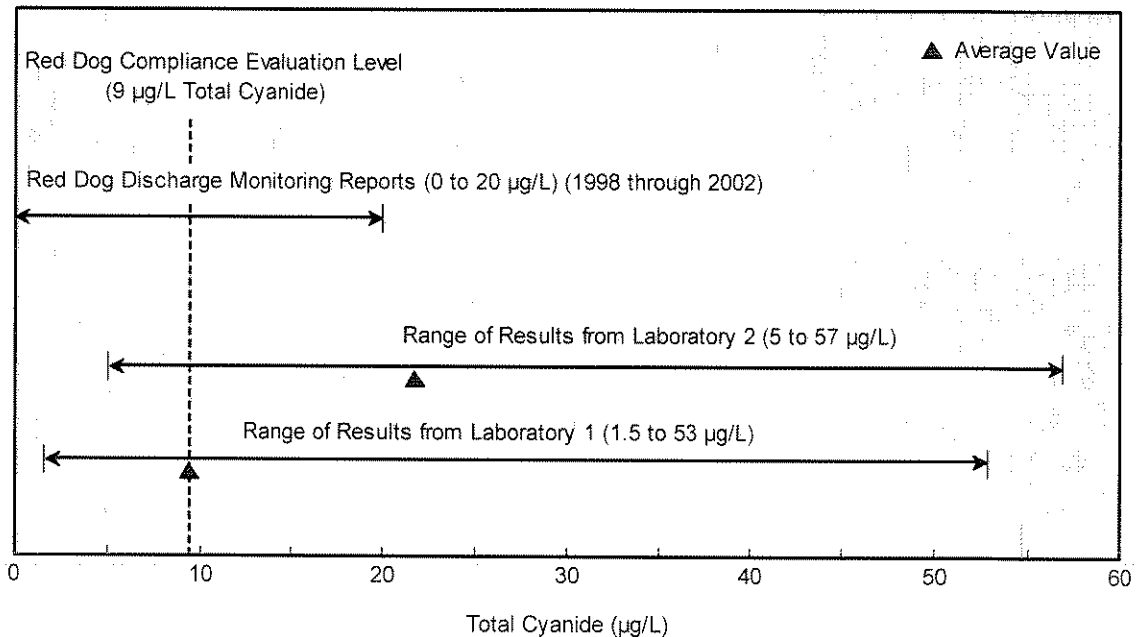



Figure 3  
Study on the Variability of Total Cyanide Analyses for Outfall 001 Split Samples

23. Based on the high level of analytical variation observed with Outfall 001 samples, development of a Method Detection Limit and Minimum Level (or Interim Minimum Level) for total cyanide would be warranted for the Red Dog site. EPA has established procedures by which the Method Detection Limit and Minimum Level can be derived.

24. Using data provided to me by Teck Cominco from their 2003 cyanide analytical study, I utilized EPA procedures to calculate Method Detection Limits and Minimum Levels for the two laboratories that provided Teck Cominco with NPDES total cyanide analytical data during 1998-2002. These calculations yielded Method Detection Limits for total cyanide of 22 µg/L and 28 µg/L for the two analytical laboratories. Similarly, Minimum Levels for total cyanide were calculated to be 92 µg/L and 114 µg/L for the two analytical laboratories. These values are consistent with my experience and as determined by other government agencies, including EPA.
25. Total cyanide values reported by Teck Cominco on Discharge Monitoring Reports for Outfall 001 were all 20 µg/L or less during 1998-2002. If the above calculated Method Detection Limits of 22 µg/L and 28 µg/L were utilized in the Red Dog NPDES permit, all Discharge Monitoring Report data would be less than the Method Detection Limit and would be considered "zero" according to EPA guidelines.
26. Based on the total cyanide analytical variation observed during the 2003 Teck Cominco study, it is not possible to determine whether the actual total cyanide concentration in Outfall 001 has been above or below the Compliance Evaluation Level of 9 µg/L during the period 1998 through 2002. The level of total cyanide analytical variation observed in 2003 reflects that encountered with similar previous studies conducted by Teck Cominco.

EXECUTED this 2<sup>nd</sup> day of SEPTEMBER, 2003 at SHERIDAN, WY.

  
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MICHAEL M. BOTZ



CERTIFICATE OF SERVICE

I certify that on the \_\_\_\_ day of September, 2003,  
a true and correct copy of the foregoing document  
was served via First class Mail, postage prepaid,  
on the following counsel of record:

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